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National Environmental Testing

Dayton Division

Standard Operating Procedure

Analyte or Suite: Semivolatile Organics

Methodology: Gas Chromotography/Mass Spectrometry

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Semi-volatile Organics

1. INTRODUCTION AND SCOPE

This is NET's preferred method used to determine semivolatile organic compounds in a variety of liquid and solid waste matrices. The following regulated compounds may be determined by this method, in addition to many others.

TABLE 1. Examples of Regulated Analytes Amenable by Method 8270

QC Use	Analyte	Reporting Limit Water ug/L	Reporting Limit Soil ug/Kg
Kb	Acenaphthene	10	330
I	Acenaphthene-d10	-	-
	Acenaphthylene	10	330
	Aniline	10	330
	Anthracene	10	330
	Benzidine	50	1650
	Benzo(a)anthracene	10	330
	Benzo(b)fluoranthene	10	330
	Benzo(k)fluoranthene	10	330
	Benzo(g,h,i)perylene	10	330
	Benzo(a)pyrene	10	330
	Benzyl alcohol	10	330
	Bis(2-chloroethoxy)methane	10	330
	Bis(2-chloroethyl)ether	10	330
	Bis(2-chloroisopropyl)ether	10	330
	Bis(2-ethylhexyl)phthalate	10	330
	4-Bromophenyl phenyl ether	10	330
	Butylbenzyl phthalate	10	330
	4-Chloroanaline	10	330
Ka	4-Chloro-3-methylphenol	10	330
	2-Chloronaphthalene	10	330
Ka	2-Chlorophenol	10	330
	4-Chlorophenyl phenyl ether	10	330
	Chrysene	10	330
I	Chrysene-d12	-	-
	Dibenzo(a,h)anthracene	10	330
	Dibenzofuran	10	330
	1,2-Dichlorobenzene	10	330
	1,3-Dichlorobenzene	10	330
Kb	1,4-Dichlorobenzene	10	330
I	1,4-Dichlorobenzene-d4	-	-
	3,3'-Dichlorobenzidine	50	1650
	2,4-Dichlorophenol	10	330
	Diethyl phthalate	10	330

QC Use	Analyte	Water ug/L	Soil ug/Kg
	2,4-Dimethylphenol	10	330
	Dimethyl phthalate	10	330
	4,6-Dinitro-2-methylphenol	10	330
P	2,4-Dinitrophenol	10	330
Kb	2,4-Dinitrotoluene	10	330
	2,6-Dinitrotoluene	10	330
	Di-n-butylphthalate	10	330
	Di-n-octylphthalate	10	330
	Fluoranthene	10	330
	Fluorene	10	330
Sb	2-Fluorobiphenyl	-	-
Sa	2-Fluorophenol	-	-
	Hexachlorobenzene	10	330
	Hexachlorobutadiene	10	330
P	Hexachlorocyclopentadiene	20	660
	Hexachloroethane	10	330
	Indeno(1,2,3-cd)pyrene	10	330
	Isophorone	10	330
	2-Methylnaphthalene	10	330
	2-Methylphenol	10	330
	4-Methylphenol	10	330
	Naphthalene	10	330
I	Naphthalene-d8	-	-
	2-Nitroaniline	15	495
	3-Nitroaniline	15	495
	4-Nitroaniline	15	495
	Nitrobenzene	10	330
Sb	Nitrobenzene-d5	-	-
	2-Nitrophenol	10	330
Ka/P	4-Nitrophenol	10	330
	N-Nitrosodimethylamine	10	330
	N-Nitrosodiphenylamine	10	330
Kb/P	N-Nitrosodi-n-propylamine	10	330
Ka	Pentachlorophenol	10	330
I	Perylene-d12	-	-
	Phenanthrene	10	330
I	Phenanthrene-d10	-	-
Ka	Phenol	10	330
Sa	Phenol-d6	-	-
Kb	Pyrene	10	330
Sb	Terphenyl-d14	-	-
Sa	2,4,6-Tribromophenol	-	-
Kb	1,2,4-Trichlorobenzene	10	330
	2,4,5-Trichlorophenol	10	330
	2,4,6-Trichlorophenol	10	330

QC (Quality Control) Uses:

I - Internal Standard for Quantitation
Sa - Surrogate Compound for acids
Sb - Surrogate Compound for bases/neutrals
Ka - Spiking compound for acids--8270 Only
Kb - Spiking compound for bases/neutrals--8270 Only
P - System Performance Check Compound
T - Mass Spectrometer Tuning Performance Compound

2. SUMMARY OF METHOD

This method is based upon a sample extraction (see Methods S-BNA3540.s.0, S-BNA3520B.s.0 and S-BNA3510B.s.1). This method is restricted to use by, or under the supervision of, NET analysts certified in the use of gas chromatograph-mass spectrometers (GC-MS), and skilled in the interpretation of mass spectra and their use as a quantitative tool.

Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation, identification, and quantitation of the compounds in the extract by gas chromatography-mass spectrometry.

3. SAFETY

Each employee is directly responsible for complete awareness of all health hazards associated with every chemical that he/she uses. The employee must be aware of these hazards, and all associated protective wear and spill clean-up procedures PRIOR TO THE USE of any chemical. In all cases, both the applicable Material Safety Data Sheet (MSDS) and supervisor or Safety Officer should be consulted. The employee should comply with all safety policies as presented in the NET Safety Manual. The bottle labels also provide important information that must be noted. Personnel performing this procedure may be working with flammables, poisons, toxics, carcinogens, teratogens, mutagens, and biohazards. In particular, approved gloves, safety glasses, and labcoats must be worn, and solvents will be handled in ventilated hoods, in addition to other measures prescribed by the Division. It should be noted that samples must be handled with as much (or more) care as any of the materials used in this method due to the unknown nature of their composition. Also, the equipment utilized by this method contain areas of both high temperature and voltage. Care must be taken whenever performing maintenance on these systems.

4. REAGENTS AND MATERIALS

The following equipment and materials, or their equivalent, are recommended for this method. Equipment and materials are considered equivalent if with their use, the analytical and QA/QC requirements in this SOP can be met.

4.1. Apparatus

4.1.1. Gas chromatograph-mass spectrometer system

4.1.1.1. Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splittless injection and all required accessories, including syringes, analytical columns, and gases. A Hewlett-Packard model 5890 is used.

4.1.1.2. Column - 50 m x 0.20 mm i.d., 0.33 micron film thickness 5% phenyl, methyl silicone coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.1.3. Mass spectrometer - Capable of scanning from 35 to 510 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum which meets all of the criteria in Section 6.4. SV for a 50 ng injection of decafluorotriphenylphosphine (DFTPP).

4.1.1.4. GC-MS interface - Capillary direct to source.

4.1.1.5. Data system - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC-MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Also, it must have the capacity of time stamping all data generated with the correct date and time. Absolutely no adjustment shall be made to this clock so as to mis-represent the actual date and/or time of analysis.

4.1.2 Autosampler- Hewlett Packard 7673.

4.1.3. Microsyringes - 10 uL, 100 uL, 250 uL, 500 uL and 1000 uL. Whenever possible, choose the syringe size that maximizes volume usage of the syringe for the most effective results.

4.1.4. Micropipetor- variable from 20 uL to 100 uL. VWR brand P.N. 53506-201. For standard preparation

4.1.5. Micropipetor- variable from 5 uL to 25 uL. VWR brand 53506-121. For addition of internal standards.

4.2. Reagents

4.2.1. Reagent grade chemicals should be used in all tests.

Caution: Many of the following standards are prepared in Methylene chloride (dichloromethane). Methylene chloride is a suspect carcinogen. Gloves and safety glasses should be worn to avoid contact with eyes and skin. Any use of methylene chloride that causes the release of vapors into the laboratory atmosphere should be conducted within a fume hood. Hoods are classified as designated areas when working with carcinogens.

Caution: Some of the following standards are prepared in methanol. Methanol is a toxic by ingestion, inhalation, and absorption. Gloves and safety glasses should be worn to avoid contact with eyes, and skin. Avoid inhalation by working with this solvent in a fume hood.

4.2.2. Sylon CT. Supelco catalog #3-3065M. This contains 5% dichlorodimethylsilane in toluene.

Caution: Sylon CT will react with water to release toxic hydrogen chloride gas--avoid contact with water. Highly flammable--keep away from ignition sources. Gloves and safety glasses should be worn to avoid contact with eyes, and skin. Avoid inhalation by working with Sylon CT in a fume hood.

4.2.3. Standards.

Caution: The following standards may contain one or more known or suspected carcinogens. Read all precautionary information supplied with the standards. Gloves and safety glasses should be worn to avoid contact with eyes, and skin. Any use of these standards in a manner that causes the release of vapors into the laboratory atmosphere should be conducted within a fume hood. Hoods are classified as designated areas when working with carcinogens.

4.2.3.1. Supelpreme-HC Base-Neutrals Mix 1. Supelco Catalog #4-8900M 2000 ug/mL.

4.2.3.2. Supelpreme-HC Base-Neutrals Mix 2. Supelco Catalog #4-8901M 2000 ug/mL.

4.2.3.3. Supelpreme-HC Polynuclear Aromatic Hydrocarbons Mix. Supelco Catalog #4-8905 2000 ug/mL.

4.2.3.4. Supelpreme-HC Phenols Mix. Supelco Catalog #4-8904M 2000 ug/mL.

4.2.3.5. Supelpreme-HC Benzidines Mix. Supelco Catalog #4-8906M 2000 ug/mL.

4.2.3.6. Supelpreme-HC Hazardous Substances Mix 1. Supelco Catalog #4-8907M 2000 ug/mL.

4.2.3.7. Supelpreme-HC Hazardous Substances Mix 2. Supelco Catalog #4-8908M 2000 ug/mL.

4.2.3.8. Pyridine. Supelco Catalog #4-8305M 2000 ug/L.

4.2.3.9. Supelpreme-HC Internal Standards Mix. Supelco Catalog #4-8902M 2000 ug/mL.

4.2.3.10. DFTPP + pentachlorophenol Supelco Catalog 4-8728M 250 ug/mL and Benzidine Supelco Catalog 4-8725M 500 ug/mL.

4.2.3.11. NET Custom Surrogate Solution. Supelco Quote #1441 2500 ug/L BN, 5000 ug/L acids.

4.3. Standard Reagents and Preparation

4.3.1. Standards storage. All standard solutions will be stored in a Teflon-sealed screw cap bottle with minimal headspace, at -10°C to -20°C and protected from light. These may not be stored in the same refrigerator with VOA standards or extracts. Storing extracts at these temperatures will cause some of the components to precipitate. ALWAYS sonicate standard solutions prior to removing aliquots to ensure all components are dissolved. Sonicate for 1 to 3 minutes depending upon the volume of the standard. Visually inspect the standard for precipitate and continue to sonicate if any is present.

4.3.2. Manufacturers of standards sometimes will change the concentration and composition of standards. ALWAYS read the literature provided with the standard so that the concentration and composition of the working standard is known. Whoever creates a standard is responsible for informing other analysts of changes in the standard concentration or composition. Each analyst in turn is responsible for ensuring that calibration and ID file(s) are correct. Prior to creating each standard the analyst should calculate the final concentration of the standard. Do not use the volumes recorded in the standard logbook for the previous standard and assume the volumes required are the same.

4.3.3. Internal Standards. Using 4.2.3.9, break the ampule and transfer into a new 1.5 mL, silanized amber autosampler vial. Include all pertinent information for this standard in your

Standards Log Book. Label each vial with the date, standard name, concentration, Standards Log Book Number and your initials. Each 1mL BNA sample extract should be spiked with 20 uL of the ISTD mix using a 25 uL syringe or micropipet. The final concentration of internal standards will be 40 mg/L in the extract.

4.3.4. Surrogate Standards. Surrogates are added during the extraction process. The concentration in 1.0 L of water is 100 ug/L for base-neutrals, and 200 ug/L for acid compounds. The concentration in the 1.0 mL extract for a 1 L water sample is 100 mg/L for the base-neutral surrogates and 200 mg/L for the acid surrogates. Percent recovery results are calculated using these values. Seventy percent recovery of a base neutral surrogate is equal to 70 mg/L in the extract. See the appropriate extraction method for preparation and use of this solution. The surrogate standard is also used for initial and continuing calibration of the BNA instrument. Surrogates are added to all Quality Control and client samples.

4.3.5. Initial Calibration Verification Standard (ICVS). The ICVS is a standard analyzed immediately after an initial calibration curve to verify the calibration solution. The ICVS mother solution is identical to the Mother Solutions in Section 4.3.6., but, must be from a different source than the Mother Solutions. If a second source is not available, use a different lot number as an ICVS. If a second source or lot number is not available, ICVS analysis is not required. Every effort should be made to obtain ICV standards. Supelco standards may be used as ICVS. Analyze the ICVS at 50 mg/L. Use instructions for the working calibration standards, section 4.3.7, to create the 50 mg/L solution.

4.3.6. Mother Solution Calibration Standards

4.3.6.1 Prepare the two mother solutions described by Tables 2 and 3 by adding the specified amounts to 5.0 mL volumetric flasks and diluting to mark with methylene chloride. Use a 1.0 mL syringe with a fixed needle or a micropipet to add these volumes.

Table 2

B/N Mother Solution (#1)	Catalog	Amount
Supelpreme-HC Base-Neutrals Mix-1	4-8900M	1.0 mL
Supelpreme-HC Base-Neutrals Mix-2	4-8901M	1.0 mL
Supelpreme-HC Benzidines Mix	4-8906M	1.0 mL
Supelpreme-HC Hazardous Substances Mix-2	4-8908M	1.0 mL

Diluted to 5.0 mL with Methylene chloride. Invert to mix.

Table 3

Acid/Aromatic Mother Solution (#2)	Catalog	Amount
Supelpreme-HC Phenols Mix	4-8904M	1.0 mL
Supelpreme-HC PNA Mix	4-8905M	1.0 mL
Supelpreme-HC Hazardous Substances Mix 1	4-8907M	1.0 mL
NET Custom BNA Surrogate Solution	NET#1441	0.8 mL
Pyridine	4-8305M	1.0 mL

Diluted to 5.0 mL with Methylene chloride. Invert to mix.
* Only if pesticides will be analyzed by GC-MS.

4.3.6.2. The final concentration of these solutions is 400 mg/L except for the acid surrogate compounds which are at 800 mg/L.

4.3.6.3. Transfer each of the above solutions to amber silanized vials. Enter all pertinent information into your Standards Log Book and identify the vials with the ID number, date prepared and descriptor (BN Mother Solution or Acid Mother Solution as appropriate). As the standards are used transfer them to smaller silanized vials to reduce the amount of headspace in the vial. Discard the standard after six months.

4.3.7. Working Standards for Initial and Continuing Calibration

4.3.7.1. Prepare working standards as described by Table 4. Use the amount listed for each standard and dilute to 1 mL with Methylene chloride. Add 20 uL of internal standard to each 1.0 mL working standard. If desired, the standard can be prepared at a volume of 0.5 mL, using one half the amounts listed in Table 4. This will conserve on the mother solutions. Add 10 uL of internal standard to each 0.5 mL working standard.

Table 4

BNA Working Standards (FV=1.0 mL)						
Solution	10 mg/L	20 mg/L	50 mg/L	80 mg/L	100 mg/L	120 mg/L
#1	25 uL	50 uL	125 uL	200 uL	250 uL	300 uL
#2	25 uL	50 uL	125 uL	200 uL	250 uL	300 uL
#4-8902M	20 uL	20 uL	20 uL	20 uL	20 uL	20 uL

All final volumes 1.0 mL. Diluting solvent Methylene chloride.

4.3.7.2. Transfer the above solutions to 1.5mL, silanized, amber vials. Enter all pertinent information into your Standards Log Book. Label the vial with the NET Standard Number, date prepared and descriptor (SSTDXXX, where XXX is the concentration; eg, SSTD020).

4.3.8. Matrix Spike, MVS, LCS Solution(s)

The solutions used for matrix spiking, Laboratory Control Standard (LCS), and Method Validation Study (MVS) analysis are identical in composition and concentration to the solutions described in section 4.3.5. The solution used as the Mother Solution, the Matrix Spike, the LCS, and the MVS can (and should) be a single solution. This solution may be split into several vials, each for a different purpose. The use and purpose of each is described below. Use instructions for creating the solutions in section 4.3.6.. Increase the standard volume as necessary. A solution different from the Mother Solution may be used as the matrix spike, LCS, and MVS if standard volume is limited.

4.3.8.1. Matrix Spikes. Matrix spikes are spiked client samples. This differs from Laboratory Control Standards (Section 4.3.8.3) which are spiked reagent water. The spikes are added as a part of the extraction process. The concentration of the matrix spike analytes in 1 L of sample is 100 ug/L (ppb) for all compounds. When the sample is concentrated to 1 mL the concentration in the extract is 100 ug/mL (ppm). See the appropriate extraction method for the preparation and use of these solutions. The matrix spikes must contain all reported analytes which are present in Table 1.

4.3.8.2. Method Verification Standard (MVS). The MVS is used to validate the analytical method. The standard must be extracted from four replicate 1 liter volumes of reagent water concentrated to a final volume of 1mL. The concentration of the analytes in 1 L of water is 100 ug/L (ppb) for all compounds. When the water is concentrated to 1 mL the concentration in the extract is 100 ug/mL (ppm). The MVS must contain all reported analytes which are present in Table 1.

4.3.8.3. Laboratory Control Standard (LCS). The LCS is a 1 liter volume of spiked reagent water which is extracted along with a sample batch and concentrated to a final volume of 1.0 mL. The concentration of the analytes in 1 L of water is 100 ug/L (ppb) for all compounds. When the water is concentrated to 1 mL the concentration in the extract is 100 ug/mL (ppm). The LCS is used to evaluate the MS/MSD results when MS/MSD recovery limits are exceeded.

4.3.9. Tuning standard A 50 mg/L solution of decafluorotriphenylphosphine (DFTPP) is utilized to verify that the GC-MS system is properly tuned (normally with PFTBA). Pentachlorophenol and benzidine are added to assess system performance prior to analyzing the standard(s).

4.3.9.1. Prepare the Tuning Standard solution. Dilute 1000 uL of the DFTPP and pentachlorophenol solution, #4-8728M, and dilute 1000 uL of the benzidine solution #4-8725M per 5 mL of Methylene chloride. The DFTPP and pentachlorophenol will be at a concentration of 50 ug/mL and benzidine will be at a concentration of 100 ug/mL.

4.3.9.2. Log this solution into the Standards Log Book. Transfer this solution to a 50 mL vial. Store this solution in vials with a Teflon lined screw-cap. Label the vial with the Standard ID Number, date prepared and descriptor (ie, DFT050).

4.3.9.3. Transfer an aliquot of this solution to a 1.5 mL vial as necessary for analysis. It need not be quantitatively measured. Enough solution must be in the vial so that the autosampler syringe needle can reach the solution.

5. INTERFERENCES

5.1. Raw GC-MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

5.2. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Methanol is recommended if the BNA instrument is in the same room as a VOA instrument, otherwise Methylene chloride should be used. Setting the autosampler for 5 to 10 rinses will usually take care of this problem.

5.3. The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, a-BHC, g-BHC, endosulfan I and II, and endrin are subject to decomposition. Therefore, for these pesticides, the use of the BNA extract for quantitation will give either low or false negative results and is therefore unacceptable. The use of method 8270 for pesticide analysis is not recommended. Method 8080 is preferred for pesticide analysis. Use of 8270 is appropriate for confirmation of pesticides at 10 ug/mL, or above, in the extract. Neutral extraction should be performed if these compounds are expected.

Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material. See the Injection Port and Column Maintenance SOP M100.

6. ANALYTICAL PROCEDURE

6.1. Sample Collection, Preservation, and Handling

6.1.1. Aqueous samples must be stored in 1 to 2.5 liter amber glass jars with Teflon liners and must be stored at 4°C. Aqueous samples must be extracted within 7 days of sample collection. If the client indicates that residual chlorine is present, each sample must additionally be preserved with 3mL/1-gal of 10% sodium thiosulfate.

6.1.2. A non-aqueous sample must be stored in a 8-oz widemouth jar with a Telfon lined lid and must be stored at 4°C. Non-aqueous samples must be extracted within 14 days of collection.

6.1.3. All extracts must be analyzed within forty days from date of extraction. The date of extraction is the date the extraction is begun.

6.1.4. Extract cleanup - Extracts containing high levels of sulfur may be cleaned up by Method 3660 using tetrabutylammonium-sulfite. Clean-up of soil extracts with a gel permeation column (GPC) is recommended to remove non-chromatographable material and long-chained hydrocarbons. Dark colored water extracts and those from municipal waste water treatment facilities may also be cleaned by GPC. If GPC is not available, dilute dark extracts with Methylene chloride.

6.2. Recommended GC-MS Operating Conditions

Table 5

Mass Spectrometer Conditions	
Electron Energy:	70 Volts (nominal)
Mass range:	35-514 amu
Scan time:	1.3 seconds per scan Sampling = 2

Table 6

Gas Chromatograph Conditions	
Initial Column temperature:	50°C
Initial Column holding time:	5.0 Minutes
Rate 1:	18°C/minute
Final Temperature 1:	100°C
Final Time 1:	0 Minutes
Rate 2:	10°C/minute
Final Temperature 2:	200°C
Final Time 2:	0.0 Minutes
Rate 3:	20°C/minute
Final Temperature 3:	340°C
Final Time 3:	10.0 Minutes (until benzo(g,h,i)perylene has eluted)
Injector temperature:	250°C
Interface:	280°C
Injector:	Split/Splittless Style, cleaned, baked and silanized
Sample volume:	1.0 uL
Carrier gas:	Helium at 25 cm/sec set at 280°C
Splittless Time:	0.3 Minutes

6.2.1. Injection Port Inertness. Due to the lability of many of the analytes analyzed by this method every attempt must be made to ensure that the analyte path in the GC is free from sites of adsorption or activity.

6.2.2. Each GC-MS system must be tuned to meet the criteria in Form-V SV for a 50ng injection of DFTPP. Analyses can not begin until all these criteria are met. Background subtraction will be straightforward and designed only to eliminate column bleed or instrument background ions. Use of a temperature program which will speed the DFTPP analysis is recommended. This will increase the number of injections possible within the 12 hour period. The following program is recommended:

DFTPP Temperature Program	
Initial Temperature	150°C
Hold Time	4 min
Ramp Rate	18°C/min
Final Temperature	280° C
Hold Time	3 min
Runtime (until Benzidine has eluted)	14 min

6.3 Method Validation Study (MVS).

6.3.1. This method must be validated by demonstrating that precision and accuracy limits in Table 7 can be met for the compounds listed in Table 7. Analytes in addition to those listed in Table 7 should be spiked but there are no precision or accuracy limits at this time. We may determine limits from the MVS data generated for these analytes. Use professional judgement in evaluating the results for these analytes.

6.3.2. Each instrument used to perform this method must be validated by analysis of four replicate MVS standards (4.3.8.2). Each analyst performing this analysis must analyze a MVS set. Each analyst is not required to perform MVS analysis on every instrument they use for analysis. Validation should be repeated whenever a significant change in the methodology or equipment is made which would render the previous MVS invalid. For example, upgrading to an on-column injection port system would require re-validation. Installing an identical column to the previous one would not require re-validation.

6.3.3. Four replicate 1 liter volumes of reagent water containing 100 ug/L of all analytes must be extracted and concentrated to a final volume of 1 mL. Calculate the mean concentration (x) and standard deviation (s) of each analyte. Quantitate the MVS standards with the daily calibration standard or the 50 mg/L point of a curve. The s and x values must be within the limits listed in Table 7.

TABLE 7

MATRIX SPIKE AND QC CHECK STANDARD ACCEPTANCE CRITERIA
SPIKE LEVEL 100UG/L

Analyte	s Limit (ug/L)	x Range (ug/L)	p Range (ug/L)
Acenaphthene*	27.6	60.1-132.3	47-145
Acenaphthylene	40.2	53.5-126.0	33-145
Anthracene	32.0	43.4-118.0	27-133
Benzo(a)anthracene	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	32.3	25.2-145.7	11-162
Benzo(a)pyrene	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	58.9	D-195.0	D-219
Benzyl butyl phthalate	23.4	D-139.9	D-152
Bis(2-chloroethyl)ether	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl)phthalate	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	23.0	64.9-114.4	53-127
2-Chloronaphthalene	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	33.4	38.4-144.7	25-158
Chrysene	48.3	44.1-139.9	17-168
Dibenzo(a,h)anthracene	70.0	D-199.7	D-227
Di-n-butyl phthalate	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene*	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	71.4	8.2-212.5	D-262
Diethyl phthalate	26.5	D-100.0	D-114
Dimethyl phthalate	23.3	D-100.0	D-112
2,4-Dinitrotoluene*	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	29.6	68.1-136.7	50-158
Di-n-octylphthalate	31.4	18.6-131.8	4-146
Fluoranthene	20.7	71.6-108.4	59-121
Hexachlorobenzene	24.9	7.8-141.5	D-152
Hexachlorobutadiene	26.3	37.8-102.2	24-116
Hexachloroethane	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	44.6	D-150.9	D-171
Isophorone	63.3	46.6-180.2	21-196
Napthalene	30.1	35.6-119.6	21-133
Nitrobenzene	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine*	55.4	13.6-197.9	D-230
Phenanthrene	20.6	65.2-108.7	54-120
Pyrene*	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene*	28.1	57.3-129.2	44-142

TABLE 7 Continued

MATRIX SPIKE AND QC CHECK STANDARD ACCEPTANCE CRITERIA
SPIKE LEVEL 100UG/L

Analyte	s Limit (ug/L)	x Range (ug/L)	p Range (ug/L)
4-Chloro-3-methylphenol	37.2	40.8-127.9	22-147
2-Chlorophenol	28.7	36.2-120.4	23-134
2,4-Chlorophenol	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	93.2	53.0-100.0	D-132
2-Nitrophenol	35.2	45.0-166.7	29-182
4-Nitrophenol	47.2	13.0-106.5	D-132
Pentachlorophenol	48.9	38.1-151.8	14-176
Phenol	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	31.7	52.4-129.2	37-144

s= standard deviation, not %RSD
x= mean concentration
p= percent recovery
D= detected
*= 8270 matrix spike compounds, all compounds must be spiked.

6.4 Initial Calibration

6.4.1. DFTPP MS Tune Criteria

Prior to the analysis of Initial Calibration Standards the GC-MS system must meet DFTPP criteria listed below. All analyses must be injected within 12 hours of the injection time of the DFTPP Standard. The DFTPP spectrum which passes the criteria must be saved to disk and archived on magnetic tape. If any addition or subtraction was utilized to generate the spectrum, the scan numbers used must be recorded in the GC-MS log book with the corresponding data file entry. It is acceptable to analyze samples subsequent to the analysis of the Calibration Standards so long as the curve is in-control and the samples are analyzed within the 12 hours from the injection of the DFTPP.

DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP) CRITERIA

m/e	ION ABUNDANCE CRITERIA
51	30.0-60.0% OF MASS 198
68	LESS THAN 2.0% OF MASS 69
69	MASS 69 RELATIVE ABUNDANCE
70	LESS THAN 2.0% OF MASS 198
127	40.0-60.0% OF MASS 198
197	LESS THAN 1.0% OF MASS 198
198	BASE PEAK, 100% RELATIVE ABUNDANCE
199	5.0-9.0% MASS 198
275	10.0-30.0% OF MASS 198
365	GREATER THAN 1.00% OF MASS 198
441	PRESENT, BUT LESS THAN MASS 443
442	GREATER THAN 40.0% OF MASS 198
443	17.0-23.0% OF MASS 442

6.4.2. Analyze 1.0 uL of each working calibration standard (as prepared in 4.3.7.1.).

6.4.3. Quantitate all standards and ensure that all compounds present are found by "QUANT". All "Q-Values" for the 50 mg/L point should be greater than 80. If any are less than 80 edit the method(s) to present ion ratios.

6.4.4. Update the multi-point calibration file using Enviroquant and generate a response factor report. Inspect the report to ensure that the mean relative response factor (RRF) is greater than 0.050, the limit for the SPCC compounds. The SPCCs are indicated by the "P" in Table 1. Low SPCC RRF's indicate an improperly silanized injection port or column problems. Repeat system maintenance except break off approximately 12 inches of column instead of the recommended 6 inches of column if SPCC's RRF's are less than 0.05. Repeat the curve.

6.4.5. For reference, the equation the program is using to calculate the RRF is;

Equation 1.

$$RRF = (Ax)(Cis)/(Ais)(Cx)$$

where:

Ax = Area of the characteristic ion for the compound being measured.

Ais = Area of the characteristic ion for the specific internal standard.

Cx = Concentration of the compound being measured (mg/L).

Cis = Concentration of the specific internal standard (mg/L).

6.4.6. The percent relative standard deviation (%RSD) must be less than 30% for each individual Calibration Check Compound (CCC) below. If the %RSD for any CCC is 30% or greater, the chromatographic system is too reactive for analysis. See 6.4.4 for corrective action suggestions. The relative retention times of each compound in each calibration run should agree within 0.5 minutes.

Calibration Check Compounds

Base Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

Equation 2.

$$\frac{SD * 100}{x} = \%RSD$$

%RSD = percent relative standard deviation.

x = mean of initial RFs for a compound.

SD = standard deviation of average RFs for a compound.

6.4.7 Linearity - If the %RSD of any compound is greater than 15%, the average RF cannot be used, but a calibration by linear or quadratic regression of the five point curve must be established. Use the type of regression which produces the smallest calibration error.

6.4.8. The retention times should be updated with each new curve. Use a mid-range point such as the 50 point. It is very important to ensure that the retention times being updated correspond to the correct analyte. For the data file being used to update retention times, print and review an extended report. If any analyte is mis-identified, confirm that this analyte is not mis-identified in the other points of the curve.

6.4.9. The analysis of an independent reference standard, or ICVS, is required immediately following each curve. The ICVS should be quantitated with the average response factors from the curve. If the quantitation results are not within +/- 30% of the true value notify your Supervisor. The +/-30% limit is a warning limit. No action is required. Document all ICVS results. Acceptance criteria will be established after sufficient data has been collected.

6.4.10. When performing Base Neutral (BN) Only analysis, only the BN compounds are required to be calibrated. When performing acids only analysis, only the acid compounds are required to be calibrated.

6.4.11. It is not always possible, or practical, to have all analytes calibrated in a single calibration run. If necessary it is acceptable to use two separate analyses to calibrate a single point.

6.5. Daily System Verification

The system must be verified to be in control daily. The following is the order in which a 12-hour sample analysis shift is conducted:

1) DFTPP injection- 12 hour clock begins

2) 50 mg/L Calibration Check

3) Analyze Extraction Batch Method Blank

4) Analyze LCS

5) Analyze Samples

6) Analyze MS/MSD (as provided by extraction personnel)

6.5.1 Injection of 50 ng of the DFTPP Standard (4.3.9) initiates the 12 hour sequence. All of the criteria given in section 6.4.1 must be met before sample analysis begins. The acceptable DFTPP spectrum must be saved to magnetic tape.

6.5.2. The initial calibration curve must be validated subsequent to the successful DFTPP analysis. This is accomplished by analyzing a 50 mg/L BNA continuing calibration standard and meeting the following criteria:

6.5.2.1. The criteria of 0.05 minimum RRF must be met for the SPCC compounds.

6.5.2.2. The maximum percent drift limit of 20% must be met for all CCC compounds listed in Section 6.4.6. Calculate percent drift as:

$$\% \text{ Drift} = \frac{Ci - Cc}{Ci} \times 100$$

where

Ci = CCC Standard Concentration
Cc = Measured Concentration using selected quantitation method.

6.5.2.3. If the retention time for any internal standard changes by more than 30 seconds from the previous Calibration Check Standard (or the average retention time from the Initial Calibration if the Check Standard is the first Check Standard since generation of the curve) the chromatographic system must be inspected for malfunctions and corrections must be made. In addition if the EICP for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

6.5.3. If the system fails to meet the criteria in 6.5.2. performing column maintenance is recommended followed by re-analysis of the check standard. If all of the criteria in 6.5.2. cannot be met, upon re-analysis of the check standard, the instrument must be recalibrated as in 6.4.

6.5.4. The method blank should contain no target analytes, except phthalates, above the reporting limit. Phthalates may be detected at up to 5 times the reporting limit. The method blank must be analyzed prior to the samples and preferably in the same analytical batch. The blank is required to be analyzed on the same instrument as the samples. If surrogate or internal standard limits for the blank are exceeded, reanalysis is required. If reanalysis is not acceptable, than re-extraction is

required. If any compound, including phthalates, is detected above the RL and can not be re-extracted or reanalyzed, the data must be flagged on the sample analysis report. Any data thus flagged will indicate possible laboratory contamination with the Blank result included.

6.5.5. Matrix spike/matrix spike duplicate analysis is required as supplied by extraction personnel. A MS/MSD set is required per batch of 20 samples or less, per matrix, per extraction technique.

6.5.6. Laboratory Control Standard analysis is required as supplied by extraction personnel. One LCS must be prepared with each extraction batch.

6.6 Sample Analysis

6.6.1. Matrix spike and surrogate recovery limits for soil and water may not be required by this SOP to be applied to industrial waste samples high in organic matter. Requirements in the following sections for reanalysis or re-extraction do not apply when the limits have been determined to be inappropriate for the matrix.

6.6.2. All samples must be injected within 12 hours of the DFTPP injection.

6.6.3. Samples should be analyzed following the Continuing Calibration.

6.6.4. Recovery limits for soil and water are listed in the Bench section of this SOP for both (Water) and (Soil) for acid and base neutral surrogates. If any surrogate is not within the surrogate limit, the sample must be reanalyzed. If it is suspected that a matrix problem affected the surrogate recovery, the reanalysis may be performed at a dilution. If upon reanalysis the surrogate(s) recovery is outside of the control limits, the sample must be re-extracted and reanalyzed if sufficient sample volume remains. Re-extraction may be performed with a lesser amount of sample than the original extraction. After re-extraction analyze the sample only once. If surrogate recoveries for the re-extracted sample are outside of limits do not reanalyze the sample again. Submit the original and reanalysis data for review.

6.6.5. The upper calibration limit is 120 mg/L in the extract. Dilution is required for analyte concentrations above 120 mg/L in the extract. Dilutions should be made so that the the analyte with the greatest concentration is in the upper half of the calibration curve.

6.6.6. When diluting sample extracts the surrogates must be multiplied by the dilution factor to calculate the surrogate recovery. It is possible that surrogates will be diluted to the point that they will not be detected and the surrogate recoveries can not be calculated. In this case surrogate recovery limits do not apply. Indicate on Quantitation report that surrogates were "diluted out".

6.6.7. Internal standard areas must be -50% to +100% of the continuing calibration internal standard areas. If internal standard standard areas are outside of these limits, the sample must be reanalyzed once. Reanalysis of a new aliquot of sample spiked with internal standard is acceptable. If it is suspected that a matrix problem effected the internal standard areas the reanalysis may be performed at a dilution. Submit both sets of data for review.

6.6.8. When diluting sample extracts, calculate the amount of internal standard that is required to bring the internal standard concentration to 40mg/L. For example, if a sample is diluted 1:10, the amount of internal standard in the extract would be 4 mg/L. An additional 36mg/L is required. To bring the internal standard concentration up to 40 mg/L, 18 uL per mL of internal standard (item 4.2.3.9) is required.

6.6.9. Serious matrix problems can effect internal standard and surrogate recoveries in ways that are difficult to reproduce. If upon reanalysis, different parameters are outside of limits, do not reanalyzed the sample again without contacting your Supervisor.

6.6.10. If either the MS or MSD do not meet the recovery limits p, in Table 7, the LCS standard must be evaluated. Only the analyte(s) which exceeded the p limit are required to be evaluated in the LCS. If the LCS standard results for the analyte of concern meet the limit p, all corresponding sample results are reportable.

6.6.11. If the LCS results do not meet the limit p, for the analyte of concern, the results for that analyte are not reportable in the corresponding samples.

6.6.12. If it is suspected there is a calibration problem, recalibrate and reanalyze the LCS. If upon reanalysis the LCS meets the limit p for the analyte of concern, reanalyze the samples and MS/MSD, and report the results.

6.6.13. If after recalibrating, LCS results are again outside of the limits, a problem exists with the analysis and a CAR is required. The problem must be investigated and corrected. Analyze a LCS to confirm the problem has been corrected.

6.6.14. After the successful analysis of a LCS standard, the samples and MS/MSD can be re-extracted and reanalyzed. With each re-extraction batch include a LCS. There may not be enough volume of the original matrix spike sample to permit performing the matrix spiking on the same sample. In this case it is acceptable to spike a different sample.

6.6.15. For samples, if the retention time for any Internal Standard changes more than 30 seconds from the last Calibration Check Standard (or the average retention time from the initial calibration if the sample is on the same run as the calibration), then the sample must be repeated to verify the matrix problem. If the problem is an instrument problem, then all associated samples with out of control retention times must be repeated once the problem has been corrected.

6.7. Data Interpretation

The qualitative and quantitative analysis for the compounds in Table 1 shall be performed primarily through the use of manufacturer supplied identification-quantitation routines. The report generated should in all but the most extreme cases allow the GC-MS operator to validate the data strictly by the information supplied in the quantitation report.

6.7.1. GC-MS-DS Sample Reports

6.7.1.1. The report for a sample shall include:

1) A summary page. Included in the header information on this page shall be the date and time of analysis. This information should be automatically included by the data system and not entered by the analyst. Also appearing should be the Lab Name and Instrument ID. This information is entered into the "Method" as the title.

For each sample input appropriate information. In the "Name" field should appear the laboratory sample number. If necessary, enter the client's sample ID into the "Miscellaneous" field. Follow it by the sample final volume, any dilution factor, extraction method, and extraction date. Following this information shall be a listing of all hits, including internal and surrogate standards. Included here should be the quantitation ion used, retention time, area and calculated concentration. The above listed information is presented in a "short" quantitation report.

2) A Total Ion Chromatogram. This should appear on two pages for BNA analyses. The peaks should be labeled with the compound number. A "summary" report will provide the information in item 1 (above) and a Total Ion Chromatogram.

3) Information for each hit should appear on a separate page. Information included here shall be;

The reference spectrum for the hit.

The background subtracted spectrum for the hit.

The raw spectrum for the hit.

The extracted ion current profile for each ion utilized to quantitate and confirm each hit.

A "Full" report will provide the information in 1), 2) and 3).

6.7.1.2. Standard, and spike reports require summary reports.

6.7.1.3. Full reports are required for all samples and blanks. Each page of the full report must be reviewed by the analyst prior to reporting results. Under no circumstances will sample results be reported based on "short" report information.

6.7.2. Qualitative Analysis

6.7.2.1. An analyte (e.g. those listed in Table 1) is identified by comparison of the sample mass spectrum with a reference mass spectrum. Reference mass spectra should be obtained on the user's GC-MS. Care must be taken when acquiring these reference spectra so as to avoid creating reference spectra from co-eluting peaks. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component and the standard component mass spectrum by visual comparison.

6.7.2.2. The RT window should be set to +/- 0.5 minutes in the ID file. To be identified the compound must be detected within this window. The Enviroquant software is unable to work with relative retention time windows (RRT), so a more typically stringent, fixed window limit of 0.5 minutes is used instead of the method requirement of 0.06 RRT units.

6.7.2.3. All ions present in the reference mass spectra at a relative intensity greater than 20% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum so long as the intensity of the peak is sufficient that those ions would be detectable.

6.7.2.4. The relative intensities of ions specified in Step 6.7.2.3. must agree within approximately 30% relative between the reference and sample spectra. (Example: For an ion with an abundance of 50% in the reference spectra, the corresponding sample abundance must be between 20% and 80%). Visual comparison is adequate.

6.7.2.5. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomer pairs.

6.7.2.6. If requested by a client, a library search may be made for the purpose of tentative identification of non-target analytes. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Guidelines for making visual identification of non-target compounds are:

(1) Relative intensities of major ions (ions > 10% of the most abundant ion) in the reference spectrum should be present in the sample spectrum. Ions less than 10% intensity may be removed by the GC-MS threshold routine and may not be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within +/- 20% relative. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

6.7.2.7. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the analyst assign a tentative identification.

6.7.2.8. It should be noted that from a mass spectrum it is frequently impossible to differentiate between isomers, particularly for aliphatic hydrocarbons and aromatics. When reporting these compounds care should be taken so as to remain consistent for a particular compound appearing in different samples from a single site or project. In the case of multiple hits of the same compound or isomer, a general description of the isomer may be reported several times. For example;

LIBRARY SEARCH SUMMARY
SEMI-VOLATILE FRACTION

SAMPLE	COMPOUND	CONCENTRATION(ug/L)
10000	Dodecane Isomer	123.
	Dodecane Isomer	92.
	Dodecane Isomer	54.

However, if the mass spectral interpretation specialist is confident that there is sufficient mass spectral uniqueness to identify a specific isomer the specific isomer should be reported.

6.7.3. Quantitative analysis of a target compound will be based on the integrated abundance of the quantitation ion as listed by Table 8. The internal standard technique will be used for quantitation. The internal standard proceeds the corresponding target analytes in Table 8.

Table 8
ISTD/TARGET COMPOUND REFERENCE INFORMATION

COMPOUND	TYPE	RT	Quant ION	Secondary Ions	
Dichlorobenzene-d4	I	8.04	152.	150.	115.
N-Nitrosodimethylamine	T	1.71	42.	74.	43.
2-Fluorophenol	S	4.21	112.	64.	92.
Aniline	T	7.33	93.	66.	65.
2-Chlorophenol	T	7.60	128.	130.	129.
bis(2-Chloroethyl)ether	T	7.67	93.	95.	
Phenol-d6	S	7.76	99.	71.	
Phenol	T	7.79	94.	66.	
1,3-Dichlorobenzene	T	7.90	146.	148.	111.
1,4-dichlorobenzene	T	8.08	146.	148.	111.
1,2-Dichlorobenzene	T	8.55	146.	148.	111.
Benzyl alcohol	T	8.75	108.	79.	51.
bis(2-Chloroisopropyl)ether	T	9.20	45.	41.	110.
2-Methylphenol	T	9.31	108.	107.	90.
Hexachloroethane	T	9.35	117.	119.	121.
N-Nitroso-di-n-propylamine	T	9.58	70.	43.	42.
4-Methylphenol	T	9.74	108.	107.	
Naphthalene-d8	I	11.38	136.	137.	
Nitrobenzene-d5	S	9.65	82.	128.	54.
Nitrobenzene	T	9.70	77.	123.	51.
Isophorone	T	10.40	82.	138.	
2-Nitrophenol	T	10.54	139.	109.	81.
2,4-Dimethylphenol	T	11.02	107.	122.	121.
bis(2-Chloroethoxy)methane	T	11.18	93.	63.	123.
2,4-Dichlorophenol	T	11.23	162.	63.	164.
1,2,4-Trichlorobenzene	T	11.33	180.	182.	184.
Naphthalene	T	11.42	128.	129.	
Benzoic Acid	T	11.71	105.	122.	
4-Chloroaniline	T	11.79	127.	129.	65.
Hexachlorobutadiene	T	12.03	225.	227.	223.
2-Methylnaphthalene	T	13.16	142.	141.	115.
4-Chloro-3-methylphenol	T	13.23	107.	144.	
Acenaphthene-d10	I	15.71	164.	162.	160.
Hexachlorocyclopentadiene	T	13.79	237.	235.	239.
2,4,6-Trichlorophenol	T	14.04	196.	198.	200.
2,4,5-Trichlorophenol	T	14.13	196.	198.	200.
2-Chloronaphthalene	T	14.32	162.	164.	127.
2-Fluorobiphenyl	S	14.25	172.	171.	170.
2-Nitroaniline	T	14.79	65.	138.	92.
Acenaphthylene	T	15.30	152.	151.	153.

ISTD/TARGET COMPOUND REFERENCE INFORMATION

COMPOUND	TYPE	RT	Quant ION	Secondary Ions	
Dimethylphthalate	T	15.49	163.	164.	194.
2,6-Dinitrotoluene	T	15.56	165.	89.	63.
Acenaphthene	T	15.79	153.	154.	152.
3-Nitroaniline	T	15.83	138.	65.	92.
2,4-Dinitrophenol	T	16.06	184.	107.	
Dibenzofuran	T	16.18	168.	139.	
2,4-Dinitrotoluene	T	16.46	165.	89.	63.
4-Nitrophenol	T	16.51	109.	139.	65.
Fluorene	T	17.01	166.	165.	167.
4-Chlorophenyl-phenylether	T	17.17	204.	141.	206.
Diethylphthalate	T	17.28	149.	177.	150.
4-Nitroaniline	T	17.35	65.	138.	92.
2,4,6-Tribromophenol	S	17.66	330.	332.	328.
Phenanthrene-d10	I	19.22	188.	189.	
4,6-Dinitro-2-methylphenol	T	17.44	198.	121.	
N-Nitrosodiphenylamine (1)	T	17.53	169.	168.	167.
4-Bromophenyl-phenylether	T	18.32	248.	250.	141.
Hexachlorobenzene	T	18.53	284.	286.	282.
Pentachlorophenol	T	19.05	266.	268.	264.
Phenanthrene	T	19.27	178.	176.	179.
Anthracene	T	19.38	178.	176.	179.
Di-n-butylphthalate	T	21.26	149.	150.	
Fluoranthene	T	22.12	202.	200.	203.
Chrysene-d12	I	24.65	240.	241.	
Pyrene	T	22.53	202.	200.	203.
Benzidine	T	22.57	184.	185.	
Terphenyl-d14	S	23.06	244.	245.	122.
Butylbenzylphthalate	T	24.08	149.	150.	206.
Benzo(a)anthracene	T	24.63	228.	229.	114.
Chrysene	T	24.70	228.	229.	114.
3,3'-Dichlorobenzidine	T	24.70	252.	254.	
bis(2-Ethylhexyl)phthalate	T	25.05	149.	167.	
Perylene-d12	I	26.68	264.	265.	
Di-n-octylphthalate	T	25.87	149.	150.	
Benzo(b)fluoranthene	T	26.13	252.	253.	250.
Benzo(k)fluoranthene	T	26.17	252.	253.	250.
Benzo(a)pyrene	T	26.59	252.	253.	250.
Indeno(1,2,3-cd)pyrene	T	28.70	276.	274.	
Dibenz(a,h)anthracene	T	28.79	278.	279.	
Benzo(g,h,i)perylene	T	29.27	276.	274.	277.

(1) Decomposes in the injection port to Diphenylamine, analyzed as such.
I = Internal Standard T = Target Compound S = Surrogate Spike Compound

6.7.3.1. Calculate the concentration of each identified analyte in the sample as follows:

Water

Equation 3.

$$\text{Concentration (ug/L)} = \frac{(C)(Vt)(1000ug/mg)}{(Vo)}$$

where:

C = Concentration as reported by "Quant" in mg/L.

C = (Ax X Cis) / (Ais X RF)

Ax = Area Sample

Cis = Conc. int. standard

Ais = Area int. standard

RF = Response factor

Vo = Volume of water extracted in mL.

Vt = Volume of total extract, taking into account dilutions (this is the effective final volume) in mL.

Sediment/Soil, Sludge, and Waste

Equation 4.

$$\text{Concentration (mg/kg)} = \frac{(C)(Vt)(0.001L/mL)}{(Ws)(0.001kg/g)}$$

where:

C, Vt, = listed above.

Ws = weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data. To convert wet weight to dry weight, multiply the weight weight by the faction solids.

6.7.3.2. Sediment/soil samples are to be be reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The % moisture of the sample should be reported along with the data in either instance.

6.7.3.3. For tentatively identified compounds, an estimate of the concentration will be made. The formulas are:

Aqueous samples

Equation 5.

$$\text{Concentration (ug/L)} = \frac{(Ax)(Is)(Vt)(1000ug/mg)}{(Ais)(RRF)(Vo)}$$

where:

Ax = Total ion area for compound being measured.

Is = Concentration of the nearest internal standard in mg/L.

Ais = Total ion area for the internal standard.

RRF = Relative response factor assumed to be 1.

Vo = Volume of water extracted (mL).

Vt = Volume of total extract in mL, taking into account dilutions.

Sediment/Soil, Sludge, and Waste

Equation 6.

$$\text{Concentration (mg/Kg)} = \frac{(Ax)(Is)(Vt)(0.001L/mL)}{(Ais)(RRF)(Ws)(0.001Kg/g)}$$

where:

Ax, Is, Ais, RRF, and Vt = same as for water.

Ws = weight of sample extracted (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

6.7.3.4. The % Dry Weight is calculated as follows:

$$\% \text{ Dry Weight} = \frac{\text{Weight of dry sample}}{\text{Weight of wet sample}} \times 100$$

6.7.3.5 The reporting limit for library search compounds is 25% of the internal standard area or 10mg/L in the extract.
6.7.3.6. Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

7. QUALITY CONTROL

Each Division that uses these methods is required to conform to the quality control program as outlined in NET's National Quality Assurance Plan. The laboratory must maintain records to document the quality of the data generated and these records will be regularly audited. The records must be complete and well organized. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method or those generated in-house that meet the minimum performance specifications of this method.

The experience of the analyst performing GC-MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still useable, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

7.1. Method Validation Study.

Method Validation Standard analysis is required. Four LCS standards at 100 ug/L must be extracted and analyzed. The standard deviation and mean concentration values must meet the limits in Table 7. MVS analysis is required to validate the analytical method. It must be repeated whenever a significant change in the method or instrumentation is made.

7.2. DFTPP Criteria.

The GC-MS system must be tuned to meet the DFTPP criteria prior to the analysis of standards, blanks, or samples. All standards, samples, blanks, and matrix spikes must be analyzed within 12

hours of DFTPP. Monitor the benzidine and pentachlorophenol response as required.

7.3. Initial Calibration Curve.

A five point curve is required for each instrument. The mean relative response factor for the SPCC compounds indicated in Table 1 must be greater than 0.050. All CCC compounds listed in 6.4.6, must have percent relative standard deviation values of less than 30%. All compounds with % RSD of greater than 15% must use calibration curves of first or higher order regression.

7.4 Initial Calibration Verification Standard

The analysis of an independent reference standard, ICVS, is required immediately following each curve. The ICVS should be quantitated using the calibration curve. If the quantitated result is not within ±40%, of the true value, it can be reanalyzed. If an acceptable ICVS can not be analyzed, the problem must be determined and corrected. A new initial calibration curve must be generated for the compounds that are out of control. Analytical results can not be accepted until an acceptable ICVS has been analyzed.

7.5. Continuing Calibration.

A 50mg/L continuing calibration standard must be analyzed for each 12 hour period. The SPCC compounds must have relative response factors of greater than 0.050. All CCC compounds must yield a % Drift of <20%. Recalibration is required if this fails.

7.6. Method Blanks.

Method blanks will be prepared by extraction personnel. A method blank should be analyzed on the same instrument as the samples extracted with it. When at all possible the method blank should be analyzed prior to the corresponding samples, and within the same batch. Analytes in Table 1 must not be detected above the Reporting Limit with the exception of phthalates. Phthalates may be detected at 5 times the reporting limit. The blank must meet internal standard and surrogate recovery limits. If these limits are exceeded, contact your Supervisor. Depending on the corresponding sample results, reanalysis and/or re-extraction may be necessary.

7.7. Internal Standards.

Internal standard areas for samples and matrix spikes must be within -50 to +100% of the continuing calibration internal standard areas. One reanalysis is required if the limit is

exceeded. Dilution is permitted if a matrix effect is suspected. Retention time must be within ±30% of the retention time from the previous CCV (or calibration if on the same run). If this criteria is not met, then the sample must be reanalyzed to verify matrix interference.

7.8. Surrogate Recoveries.

Surrogate recoveries must meet the recovery limits. If the limits are exceeded reanalysis is required. If the limits are exceeded upon reanalysis the sample must be re-extracted and reanalyzed if sufficient sample volume remains. Dilution is permitted if a matrix effect is suspected. See section 6.6.1. regarding unusual matrices.

7.9. Matrix Spikes/Matrix Spike Duplicates.

If matrix spike recovery limits in Table 7 are exceeded, the evaluation of the LCS is required. Note: although all analytes are required to be spiked, only the eleven representative compounds suggested in 8270 will be monitored by LABSYS II.

7.9.1. The calculation for accuracy is:

$$\text{Accuracy} = \frac{(\text{Spiked sample} - \text{Unspiked sample})}{\text{True Value}} \times (100)$$

7.9.2. The calculation for Precision as Relative Standard Deviation (RSD) is:

$$\text{RSD} = \frac{\text{Standard deviation of the replicates}}{\text{Mean of the replicates}} \times (100)$$

Precision (RSD) must be less than 20%.

7.10. Laboratory Control Standard (LCS).

An LCS must be extracted with each sample batch. LCS evaluation is required when the matrix spike or matrix spike duplicate results exceed the recovery limits in Table 7. If the LCS analysis results are within the recovery limits for the analyte(s) of concern, the sample results are reportable. If the LCS analysis results are outside of the limits for the analyte(s) of concern, sample results for that analyte can not be reported. The system may be recalibrated and the LCS analyzed again. If the LCS results are within the control limits, the samples and MS/MSD may be reanalyzed and reported. If after recalibrating, the LCS results are again outside the control limit, a problem exists with the analysis and a CAR is required. After the successful analysis of a LCS, the samples and MS/MSD can be

re-extracted and reanalyzed. With each re-extraction batch include a LCS. The LCS is referred to as a QC Check standard in EPA methods 8270 and 625.

7.11. In House Control Limits.

In house control limits for surrogates and laboratory control standards will be developed and updated on an annual basis.

7.12. Method Detection Limit Studies

Method Detection Limit Studies are required per the MDL SOP initially and when significant changes in the analytical method are made. Analysts should consult their supervisor about whether or not a change warrants a MDL study. Consider performing a MDL study whenever MVS analysis is required (6.3.1).

8. REFERENCES

1. USEPA SW-846, "Method 8270: Gas Chromatography - Mass Spectrometry for Semivolatile Organics", Office of Solid Waste, Revision 1, December 1987.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, 2/88.

3. "Definition and Procedure for the Determination of the Method Detection Limit", Revision 1.11, Appendix B, 40 CFR 136.

4. Federal Register Vol. 49, No. 209 Friday October 26, 1984 Method 625--Base/Neutrals and Acids.

9. Semi-Volatile SOP Bench Reference

This summary in intended for use by analysts who are familiar with SOP S-8270 Analysts are responsible for requirements in the SOP which may not be summarized here. Numbers in parentheses refer to paragraphs in the SOP where further information can be found.

12 Hour Sequence

a. DFTPP starts clock
b. Continuing Calibration or Initial Calibration
c. Method Blank
d. LCS
e. Samples
f. MS/MSD (as provided by extraction personnel)

DFTPP Analysis

12 hour clock begins with DFTPP injection time (6.5.1). An analysis method for DFTPP which has a short run time is recommended. Criteria on Form 5 (ie Tuner=DFTPP) must be met. Monitor benzidine and pentachlorophenol response and peak shape.

Initial Calibration

Calibration levels are 10, 20, 50, 80, 100 and 120 ppm. The 10ppm point for the following compounds may be dropped: benzoic acid, 2,4-dinitrophenol, 4-nitroaniline, 4-nitrophenol, 4,6-dinitro-2-methylphenol, pentachlorophenol.

SPCC compounds must have minimum RRFs of 0.05 (6.4.5).

Continuing Calibration

A 50ppm standard is analyzed after DFTPP (6.5.2). SPCCs must have RRFs > 0.05. All analytes except those listed above must have %D of < 20% (6.5.2.2). Those listed above must have %D of less than 100%.

Method Blanks

Extraction personnel will prepare a method blank. To be "in control" no analytes, except phthalates, may be detected above the RL. Phthalates may be detected at above 5X the RL (7.6.). Surrogate and internal standard limits must be met for method blanks. Blanks should be analyzed before any samples are. Whenever possible analyze the blank immediately prior to the corresponding samples. When no additional sample remains and/or the extraction or analysis can not be repeated, any hits detected in a blank and sample above the reporting limit, including

phthalates, must be flagged on the sample report.

Samples

Samples must be injected within 12 hours of the DFTPP injection (6.5.1). Samples can not be analyzed until a successful calibration has been performed (6.5.2). Surrogate recoveries must meet limits in Table 9. If limits are exceeded reanalyze the extract (6.5.3). If surrogate recoveries are outside limits again re-extract and reanalyze the sample once. Internal standard must be within -50% to +100% of the standard internal standards (6.6.6). If internal standard limits are outside of limits reanalyze the sample. Reanalysis of a new aliquot of sample spiked with internal standard is acceptable. If a matrix problem is effecting surrogate or internal standard recoveries, reanalysis of a diluted sample is acceptable. Provide initial and reanalysis results to your Supervisor for review.

MS/MSD

Extraction personnel will provide MS/MSDs for analysis. If the MS/MSD limits are exceeded, a LCS must be analyzed.

LCS Analysis

LCS are used to validate the method and evaluate matrix effects. If MS/MSD limits are exceeded, a LCS containing the analyte of concern must evaluated.

Table 9.

Surrogate Limits		
Compound	Water	Soil
Nitrobenzene-d5	35-124	23-120
2-Fluorobiphenyl	43-134	30-115
Terphenyl-d14	34-149	18-137
Phenol-d6	10-149	24-113
2-Fluorophenol	21-145	25-121
2,4,6-Tribromophenol	10-146	19-122

Internal Standard Limit

-50% to +100% of 50 ppm calibration. Retention time must be $\pm$30 seconds. Re-extract and/or reanalyze samples if either criteria can not be met.

Notes

While reviewing BNA standard and sample data, be aware that some compounds have identical or similar spectra and can be mistaken for each other. Compounds with similar spectra may or may not be isomers. Compounds which may coelute are indicated. Some compounds with similar or identical, spectra and can only be differentiated by retention time.

1,3-dichlorobenzene
1,4-dichlorobenzene > **may coelute**
1,2-dichlorobenzene

2-methylphenol
4-methylphenol

2-nitrophenol
4-nitrophenol

2,4,6-trichlorophenol
2,4,5-trichlorophenol

2-nitroaniline
3-nitroaniline
4-nitroaniline

dibenzofuran
4-nitrophenol

phenanthrene
anthracene

fluoranthene
pyrene

benzo(a)anthracene
chrysene

benzo(b)fluoranthene
benzo(k)fluoranthene > **may coelute**
benzo(a)pyrene

indeno(1,2,3-cd)pyrene
benzo(g,h,i)perylene > **may coelute**

VAP APPENDIX

The following modifications to this SOP will be applied to all samples received in support of the Voluntary Action Program (VAP).

I. When a first or second order regression curve is required for compounds exceeding 15% RSD in the initial calibration, the correlation coefficient of the curve must be at least 0.995 or recalibration is required.